WET CLEANS FOR COBALT DISILICIDE PROCESSING

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Background of the Invention

1. Technical Field

The present invention relates to a method for removing a formation of an oxide of titanium that is generated as a byproduct of a process that forms cobalt disilicide within an insulated-gate field effect transistor.

2. Related Art

Integrated circuits constructed on silicon substrates are limited in performance by the resistance of the source, drain, and gate of a field effect transistor (FET). This difficulty may be addressed by forming cobalt disilicide areas within FETs, since the cobalt disilicide areas have low electrical resistance. For example, cobalt disilicide within the source and drain of an FET lowers the total resistance for current flow from a contact, through the FET source, into the FET channel, and out of the FET drain.

In the formation of cobalt disilicide, it is well known to utilize a layer of cobalt as a source for the cobalt disilicide and to use a titanium nitride (TiN) capping layer to protect the cobalt from oxidizing during a subsequent annealing step. After a first annealing step, this sacrificial TiN capping layer is chemically removed by a selective etch with a solution such as one comprising hydrogen peroxide. Discrete portions of the TiN cap are not always removed by this process, however, and a residual configuration, or "stringer," of one or more oxides of titanium, such as titanium dioxide, may remain after the cobalt disilicide is formed in a second

annealing step. Unfortunately, the stringer of a titanium oxide is electrically conductive and may cause electrical shorting of adjacent structures. For example, the stringer may cause a short between the gate and the drain of an FET, between the source of a first FET and the drain of a second FET, or between the drain of an FET and external circuitry. The prior art does not disclose a method of removing a stringer of an oxide of titanium that is generated as described above.

Summary of the Invention

Sub> The present invention provides a method of removing an oxide of titanium which is generated as a byproduct of a process that forms cobalt disilicide within a semiconductor device such as an FET.

The present invention provides an FET within a substrate, wherein the FET is a gate-insulated field effect transistor comprising a source, a drain, a gate, a gate insulator, and a channel. Typically, the substrate is first precleaned with a suitable reagent such as hydrofluoric acid (HF). This precleaning removes a film of silicon dioxide (SiO_2) that became deposited on a surface of the layer of silicon as a consequence of prior processing or of prior exposure of the substrate to air at room temperature. Next, a layer of cobalt is formed on a top surface of the substrate by use of a sputtering process such as with argon gas in a low-pressure chamber. The top surface of the substrate comprises a portion of the top surface of each of the source, drain, gate, and insulating structures. Next, a layer of titanium nitride is formed on the layer of cobalt by use of a second sputtering process such as with argon gas and nitrogen gas in a low-pressure chamber. Then a first annealing of the substrate causes portions of the layer of cobalt to react

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with the source, drain, and gate to transform a top portion of each of the source, drain, and gate into a silicide zone comprising a greater amount of cobalt silicide (CoSi) and a lesser amount of cobalt disilicide ($CoSi_2$). Unreacted cobalt remains after the preceding annealing step, particularly on top of the isolating structures. The layer of titanium nitride and the unreacted cobalt are removed by a first cleaning with a reagent such as one comprising hydrogen peroxide and sulfuric acid. Impurities comprising titanium, cobalt, silicon, oxygen, and/or nitrogen may be present on the substrate after the first cleaning and a second cleaning is performed to remove the impurities. The first and second cleanings in combination may not successfully remove all impurities and impurities comprising titanium may be present on the substrate. Next, a second annealing process transforms cobalt monosilicide to cobalt disilicide in the silicide zone, thereby forming the desired cobalt disilicide within the FET. Nonetheless, a stringer of an oxide of titanium may be present on one or more of the cobalt disilicide areas of the silicide zone following the second annealing, and all such stringers should be removed to prevent shorting of adjacent electrical structures of, within, or coupled to, the FET. The final step removes the stringers by applying a reagent to the substrate at a suitable temperature, and for a period of time, wherein the reagent does not chemically react with the cobalt disilicide.

Use of an FET in the preceding method is illustrative. The preceding process steps may be applied to any semiconductor structure to form cobalt disilicide volumes that are free of stringers of an oxide of titanium.

Thus, the invention has the advantage of forming cobalt disilicide by a process that does not leave stringers of one or more oxides of titanium.

Brief Description of the Drawings

FIG. 1 depicts a side cross-sectional view of an oxide of titanium on the top surface of a layer of material, in accordance with a preferred embodiment of the present invention.

FIG. 2 depicts FIG. 1 with the oxide of titanium removed.

FIG. 3 depicts a side cross-sectional view of a layer of substrate comprising a layer of silicon, in accordance with a preferred embodiment of the present invention.

FIG. 4 depicts FIG. 3 with an added layer of cobalt.

FIG. 5 depicts FIG. 4 with an added layer of titanium nitride.

FIG. 6 depicts FIG. 5 following a first annealing step.

FIG. 7 depicts FIG. 6 following a first cleaning step.

FIG. 8 depicts FIG. 7 following a second cleaning step.

FIG. 9 depicts FIG. 8 following a second annealing step.

FIG. 10 depicts FIG. 9 following a third cleaning step.

FIG. 11 depicts a side cross-sectional view of a substrate comprising an FET, in accordance with a preferred embodiment of the present invention.

FIG. 12 depicts FIG. 11 with an added layer of cobalt.

FIG. 13 depicts FIG. 12 with an added layer of titanium nitride.

FIG. 14 depicts FIG. 13 following a first annealing step.

FIG. 15 depicts FIG. 14 following a first cleaning step.

FIG. 16 depicts FIG. 15 following a second cleaning step.

FIG. 17 depicts FIG. 16 following a second annealing step.

FIG. 18 depicts FIG. 17 following a third cleaning step.

Detailed Description of the Invention

In a first step of a preferred embodiment of the present invention, FIG. 1 illustrates a side cross-sectional view of a layer of material **10** having a top surface **12**, and a patch of an oxide of titanium **14**, on the top surface **12**. The patch of oxide of titanium **14** may include titanium dioxide, titanium oxide, etc. The layer of material **10** may be any material that does not chemically react with the reagent to be discussed in connection with FIG. 2. More particularly, the layer of material **10** may comprise cobalt disilicide ($CoSi_2$) such as is formed in the fabrication of semiconductor devices.

FIG. 2 depicts FIG. 1 with the oxide of titanium removed as a result of applying a reagent under suitable conditions; e.g., by immersing the layer **10** with patch **14** in a chemical reagent at a suitable temperature and period of time, wherein the reagent does not react with the layer of material **10**. A particular reagent that is effective for this removal step comprises water (H_2O), ammonium hydroxide (NH_4OH), and hydrogen peroxide (H_2O_2), wherein the NH_4OH and the H_2O_2 each comprise approximately 4% of the total reagent volume. This reagent should be applied at a temperature that is approximately in the 45 to 95 ^{0}C range for a period of time ranging approximately from 30 seconds to 10 minutes. For example, given a temperature of 65 ^{0}C, a period of time of approximately 3 minutes is effective. Generally, the minimum required period of time is inversely dependent on the applied temperature.

In a first step of a preferred embodiment of the present invention for forming a clean layer of cobalt disilicide, FIG. 3 illustrates a side cross-sectional view of a provided substrate **20** comprising a layer of silicon **22**. A precleaning with a chemical solution, such as hydrofluoric acid (HF), is typically performed prior to the first step of FIG. 3 in order to remove from the layer

of silicon **22** a film of silicon dioxide (SiO_2) that results from prior processing or from exposure of silicon to air at room temperature. The film of silicon dioxide has a thickness typically in the range of 20 to 50 angstroms.

FIG. 4 depicts FIG. 3 with an added layer of cobalt **24**. The layer of cobalt **24** may be formed on the layer of silicon **22** by any suitable technique known to those skilled in the art. For example, a cobalt sputtering process may be employed, wherein the substrate **20** is placed in a depressurized chamber containing argon (Ar) gas and a region of cobalt. A voltage applied to the chamber first causes the argon atoms to be ionized into Ar+ ions and next accelerates the Ar+ ions to move within the chamber. A percentage of the accelerated Ar+ ions strikes the region of cobalt, resulting in formation of gaseous cobalt with moving cobalt atoms, wherein a share of the moving cobalt atoms adheres to the layer of silicon **22** to form the layer of cobalt **24**, as shown in FIG. 4. While a range of thicknesses may characterize the layer of cobalt **24**, as is known to those of ordinary skill in the art, a thickness of approximately 80 angstroms is representative. The layer of cobalt **24** should be formed within approximately 2 hours after the precleaning removal of the silicon dioxide film (see discussion of FIG. 3) in order to avoid reforming a silicon dioxide film on the layer of silicon **22**.

FIG. 5 depicts FIG. 4 with an added layer of titanium nitride **26**. The layer of titanium nitride **26** may be formed on the layer of cobalt **24** by any suitable technique known to those skilled in the art. For example, a sputtering process may be employed, wherein the substrate **20** is placed in a depressurized chamber containing argon (Ar) gas, nitrogen gas, and a region of titanium. A voltage is applied to the chamber, which first causes the argon atoms to be ionized into Ar+ ions and next accelerates the Ar+ ions to move within the chamber. A percentage of the

accelerated Ar+ ions strikes the region of titanium resulting in formation of gaseous titanium with moving titanium particles, wherein a share of the moving titanium particles strikes and combines with the nitrogen gas to form titanium nitride particles, and wherein a share of the titanium nitride particles adheres to the layer of cobalt **24** to form the layer of titanium nitride **26**, as shown in FIG. 5. While a range of thicknesses may characterize the layer of titanium nitride **26**, as is known to those of ordinary skill in the art, a thickness of approximately 200 angstroms is representative.

FIG. 6 depicts FIG. 5 following a first annealing step, wherein the layer of cobalt **24** and a top portion of the layer of silicon **22** (see FIG. 5) react and are transformed into a layer of silicides of cobalt **34** and a thinner layer of silicon **32** (see FIG. 6), and wherein the layer of silicides of cobalt **34** comprises a greater amount of cobalt monosilicide (CoSi) and a lesser amount of cobalt disilicide ($CoSi_2$). The mixture of cobalt monosilicide and cobalt disilicide is generally inhomogeneously distributed within the layer of silicides of cobalt **34**. While the time and temperature of the first annealing step may vary within limits known to those ordinarily skilled in the art, a temperature range of approximately 540 ^{0}C to approximately 600 ^{0}C for a time period of approximately 5 seconds to approximately 2 minutes are representative. The preceding first annealing step causes the combined thickness of the layer of silicides of cobalt **34** and the thinner layer of silicon **32** (see FIG. 6) to be less than the combined thickness of the layer of cobalt **24** and the layer of silicon **22** (see FIG. 5). While a range of thicknesses may characterize the layer of silicides of cobalt **34**, as is known to those ordinarily skilled in the art, a thickness of approximately 160 angstroms is representative.

FIG. 7 depicts FIG. 6 following a first cleaning step, which has the purpose of removing

the reconfigured layer of titanium nitride **36** (see FIG. 6) and also to remove any unreacted cobalt from the preceding first annealing step. The first cleaning step may be accomplished by use of a chemical reagent, such as one comprising hydrogen peroxide and sulfuric acid. As shown in FIG. 7, an impurity **38** comprising titanium, cobalt, and/or silicon, may be present on the layer of silicides of cobalt **34** after the first cleaning step.

FIG. 8 depicts FIG. 7 following a second cleaning step, whose purpose is to remove the impurity **38** (see FIG.7). The second cleaning step may be accomplished in the following two sub-steps. First, the substrate **20** is sprayed with a first reagent at a temperature of approximately 40 ^{0}C, wherein the first reagent comprises water, ammonium hydroxide, and hydrogen peroxide, wherein the ammonium hydroxide and the hydrogen peroxide each comprises approximately 4% of a total first reagent volume. Second, the substrate **20** is sprayed with a second reagent at a temperature of approximately 65 ^{0}C, wherein the second reagent comprises water, hydrochloric acid, and hydrogen peroxide, wherein the hydrochloric acid comprises approximately 5% of a total second reagent volume, and wherein the hydrogen peroxide comprises approximately 4% of the total second reagent volume. The second cleaning step may not successfully remove all impurities and an impurity **40** comprising titanium may be present on the layer of silicides of cobalt **34** after the second cleaning step, as shown in FIG. 8.

FIG. 9 depicts FIG. 8 following a second annealing step, wherein the cobalt silicide in the layer of silicides of cobalt **34** is transformed into cobalt disilicide, resulting in the layer of silicides of cobalt **34** (FIG. 8) being replaced by a layer of cobalt disilicide **44**, as shown in FIG. 9. Since the second annealing step involves chemical reactions involving silicon, part of the layer of silicon **32** (FIG. 8) is incorporated within the layer of cobalt disilicide **44** (FIG. 9), which

reflects a possible change in the thickness of the layer of silicon **32** (FIG. 8) to form a modified layer of silicon **33** (FIG. 9). While the time and temperature of the second annealing step may vary within limits known to those ordinarily skilled in the art, a temperature range of approximately 700 ^{0}C to approximately 850^{0}C for a time period of approximately 1 second to approximately 1 minute are representative. Generally, the minimum required period of time is inversely dependent on the temperature. Although the second annealing step forms the desired layer of cobalt disilicide **44**, an undesired stringer of an oxide of titanium **42** may be nonetheless be present on the layer of the cobalt disilicide **44** following completion of the second annealing step, as shown in FIG. 9.

FIG. 10 depicts FIG. 9 following a third cleaning step, which has the purpose of removing the stringer of an oxide of titanium **42** (see FIG. 9) in order to prevent shorting of adjacent electrical structures within, or coupled to, the substrate **20**. The third cleaning step removes the stringer **42** by applying a reagent under suitable conditions; e.g., by immersing the substrate **20** in a chemical reagent at a suitable temperature and period of time, wherein the reagent does not chemically react with the layer of cobalt disilicide **42**. A particular reagent that is effective for this removal step comprises water (H_2O), ammonium hydroxide (NH_4OH), and hydrogen peroxide (H_2O_2), wherein the NH_4OH and the H_2O_2 each comprises approximately 4% of the total reagent volume. This reagent should be applied at a temperature that is approximately in the 45 to 95 ^{0}C range for a period of time ranging approximately from 30 seconds to 10 minutes. For example, given a temperature of 65 ^{0}C, a period of time of approximately 3 minutes is effective. Generally, the minimum required period of time is inversely dependent on the applied temperature. The effect of the third cleaning step is to achieve the goal of removing the stringer

of an oxide of titanium **42**, as shown in FIG. 10.

In a first step of a preferred embodiment of the present invention for forming a clean layer of cobalt disilicide, FIG. 11 illustrates a side cross-sectional view of a provided substrate **50**, comprising an insulated-gate field effect transistor (FET) **49** and isolating structures **56** and **58**. The FET **49** comprises a source **52**, drain **54**, channel **51**, gate **142**, gate insulator **140**, and insulating spacers **144** and **146**. While the source **52**, drain **54**, and channel **51** are shown to comprise N+ , N+, and P- material, respectively, the source **52**, drain **54**, and channel **51** may alternatively comprise P+ , P+, and N– material, respectively. The insulating spacers **144** and **146** comprise any suitable electrically insulating material such as an oxide or nitride of silicon. The isolating structures **56** and **58** are any structures that electrically isolate the FET **49** such as trench isolation structures or grown oxide structures.

A precleaning of the substrate **50** with a chemical solution, such as hydrofluoric acid (HF), is typically performed prior to the first step of FIG. 11 in order to remove from a surface of the substrate **50** a film of silicon dioxide (SiO_2) that results from exposure of silicon to air at room temperature. The film of silicon dioxide has a thickness typically in the range of 20 to 50 angstroms.

FIG. 12 depicts FIG. 11 with an added layer of cobalt **60**. The layer of cobalt **60** may be formed on a top surface **61** of the FET **49** and isolating structures **56** and **58** by any suitable technique known to those skilled in the art. For example, a cobalt sputtering process may be employed, wherein the substrate **50** is placed in a depressurized chamber containing argon (Ar) gas and a region of cobalt. A voltage applied to the chamber first causes the argon atoms to be ionized into Ar+ ions and next accelerates the Ar+ ions to move within the chamber. A

percentage of the accelerated Ar+ ions strikes the region of cobalt, resulting in formation of gaseous cobalt with moving cobalt particles, wherein a share of the moving cobalt particles adheres to the top surface **61** to form the layer of cobalt **60**, as shown in FIG. 12. While a range of thicknesses may characterize the layer of cobalt **60**, as is known to those of ordinary skill in the art, a thickness of approximately 80 angstroms is representative. The layer of cobalt **60** should be formed within approximately 2 hours after the precleaning removal of the silicon dioxide film (see discussion of FIG. 11) in order to avoid reforming a silicon dioxide film on the top surface **61**.

FIG. 13 depicts FIG. 12 with an added layer of titanium nitride **62**. The layer of titanium nitride **62** may be formed on the layer of cobalt **60** by any suitable technique known to those ordinarily skilled in the art. For example, a sputtering process may be employed, wherein the substrate **50** is placed in a depressurized chamber containing argon (Ar) gas, nitrogen gas, and a region of titanium. A voltage is applied to the chamber, which first causes the argon atoms to be ionized into Ar+ ions and next accelerates the Ar+ ions to move within the chamber. A percentage of the accelerated Ar+ ions strikes the region of titanium resulting in formation of gaseous titanium with moving titanium particles, wherein a share of the moving titanium particles strikes and combines with the nitrogen gas to form titanium nitride particles, and wherein a share of the titanium nitride particles adheres to the layer of cobalt **60** to form the layer of titanium nitride **62**, as shown in FIG. 13. While a range of thicknesses may characterize the layer of titanium nitride **62**, as is known to those of ordinary skill in the art, a thickness of approximately 200 angstroms is representative.

FIG. 14 depicts FIG. 13 following a first annealing step, wherein the layer of cobalt **60**

reacts with a top portion of the source **52**, drain **54**, and gate **142** (see FIG. 13) to form layers of silicides of cobalt **82**, **84**, and **90**, respectively (see FIG. 14), comprising a greater amount of cobalt silicide (CoSi) and a lesser amount of cobalt disilicide ($CoSi_2$). The mixture of cobalt silicide and cobalt disilicide is generally inhomogeneously distributed within the layers of silicides of cobalt **82**, **84**, and **90**. Also, the source **52**, drain **54**, and gate **142** (see FIG. 13) are geometrically transformed into source **72**, drain **74**, and gate **92**, respectively (see FIG. 14). Non-reacting cobalt remain in cobalt layers **86** and **88**. The first annealing step also reconfigures the layer of titanium nitride **62** (see FIG. 13), into the layer of titanium nitride **63** (see FIG. 14). While the time and temperature of the first annealing step may vary within limits known to those ordinarily skilled in the art, a temperature range of approximately 540 ^{0}C to approximately 600 ^{0}C for a time period of approximately 5 seconds to approximately 2 minutes are representative While a range of thicknesses may characterize the layers of silicides of cobalt **82**, **84**, and **90**, as is known to those ordinarily skilled in the art, a thickness of approximately 160 angstroms is representative.

FIG. 15 depicts FIG. 14 following a first cleaning step, whose purpose is to remove the layer of titanium nitride **63** (see FIG. 14) and also to remove cobalt layers **86** and **88** as well as any additional unreacted cobalt from the preceding first annealing step. The first cleaning step may be accomplished by use of a chemical reagent, such as one comprising hydrogen peroxide and sulfuric acid. As shown in FIG. 15, impurities **100** and **102**, comprising titanium, cobalt, and/or silicon, may be present after the first cleaning step.

FIG. 16 depicts FIG. 15 following a second cleaning step, which has the purpose of removing the impurities **100** and **102** (see FIG. 15). The second cleaning step may be

accomplished in the following two sub-steps. First, the substrate **50** is sprayed with a first reagent at a temperature of approximately 40 ^{0}C, wherein the first reagent comprises water, ammonium hydroxide, and hydrogen peroxide, wherein the ammonium hydroxide and the hydrogen peroxide each comprises approximately 4% of a total first reagent volume. Second, the substrate **50** is sprayed with a second reagent at a temperature of approximately 65 ^{0}C, wherein the second reagent comprises water, hydrochloric acid, and hydrogen peroxide, wherein the hydrochloric acid comprises approximately 5% of a total second reagent volume, and wherein the hydrogen peroxide comprises approximately 4% of the total second reagent volume. The second cleaning step may not successfully remove all impurities and the impurities **110** and **112** comprising titanium may be present after the second cleaning step, as shown in FIG. 16.

FIG. 17 depicts FIG. 16 following a second annealing step, wherein the cobalt silicide in the layers of silicides of cobalt **82**, **84**, and **90** is transformed into cobalt disilicide, resulting in the layers of silicides of cobalt **82**, **84**, and **90** (FIG. 16) being replaced by a layers of cobalt disilicide **83**, **85**, and **91**, respectively (FIG. 17). Since the second annealing step relates to chemical reactions involving silicon, the source **72**, drain **74**, and gate **92** (FIG. 16) are geometrically changed into source **73**, drain **75**, and gate **93**, respectively (FIG. 17). Gate **92** (FIG. 16) is changed to gate **93** (FIG. 17), which reflects a possible repositioning of gate **92**. While the time and temperature of the second annealing step may vary within limits known to those ordinarily skilled in the art, a temperature range of approximately 700 ^{0}C to approximately 850^{0}C for a time period of approximately 1 second to approximately 1 minute are representative. Generally, the minimum required period of time is inversely dependent on the temperature. Although the second annealing step forms the desired layers of cobalt disilicide **83**, **85**, and **91**,

undesired stringers of an oxide of titanium **120** and **122** may be nonetheless be present following completion of the second annealing step, as shown in FIG. 17.

FIG. 18 depicts FIG. 17 following a third cleaning step, which ha the purpose of removing the stringers of an oxide of titanium **120** and **122** (see FIG. 17) in order to prevent shorting of adjacent electrical structures within, or coupled to, the FET **49**. The third cleaning step removes the stringers **120** and **122** by applying a reagent under suitable conditions; e.g., by immersing the substrate **50** in a chemical reagent at a suitable temperature and period of time, wherein the reagent does not chemically react with the layers of cobalt disilicide **83**, **85**, and **91**. A particular reagent that is effective for this removal step comprises water (H_2O), ammonium hydroxide (NH_4OH), and hydrogen peroxide (H_2O_2), wherein the NH_4OH and the H_2O_2 each comprises approximately 4% of the total reagent volume. This reagent should be applied at a temperature that is approximately in the 45 to 95 ^{0}C range for a period of time ranging approximately from 30 seconds to 10 minutes. For example, given a temperature of 65 ^{0}C, a period of time of approximately 3 minutes is effective. Generally, the minimum required period of time is inversely dependent on the applied temperature. The effect of the third cleaning step is to achieve the goal of removing the stringers **120** and **122**, as shown in FIG. 18.

While preferred and particular embodiments of the present invention have been described herein for purposes of illustration, many modifications and changes will become apparent to those ordinarily skilled in the art. Accordingly, the appended claims are intended to encompass all such modifications and changes as fall within the true spirit and scope of this invention.